3 Amino Acids and Peptides

A variety of unusual amino acids and small cyclic and acyclic oligopeptides have been isolated from marine organisms. These have been the subject of intense synthesis activity due to the potent and broad spectrum of activities exhibited by the various members of this class. Syntheses of a number of bromotyrosine-derived metabolites are also included in this section.

3.1 Various Amino Acids

3.1.1 Carnosadine

Carnosadine, a new cyclopropyl amino acid isolated [312] from the red alga Grateloupia carnosa, has been synthesized by Shiba [313] as shown in Scheme 192. Dipolar cycloaddition of diazomethane to acid 1212 gives pyrazoline 1213 which upon photolysis provides cyclopropane 1214. Conversion of ester 1214 to the amide followed by Hofmann degradation gives amine 1215. Resolution of the diastereomers and addition of guanidine to 1215 gives (−)-carnosadine in 13 steps and 6.1% overall yield.

\(-\)-Carnosadine 1216

3.1.2 Ovothiols A and C

Ovothiols A and C have been synthesized by Hopkins [314] from the parent heterocycle 1217 as shown in Scheme 193. Hydroxymethylation and chlorination of 1217 gives imidazole 1219 in two steps. Treatment of 1219 with α-glycincyl anion equivalent 1220 affords amino acid 1221. Removal of the thiol
Scheme 192. Shiba Synthesis of (−)-Carnosadine

(−)-Carnosadine 1216

-established absolute configuration